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THE SECONDARY K-ABSORPTION SPECTRA OF SULPHUR*

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Plate III

Abstract. The X-ray K-absorption spectrum of Sulphur shows pronounced structure extending up to an energy distance of 87 volts from the main edge The spectrum obtained shows definitely two definite absorbing regions, and the intensity of some bands at large energy distance from the primary are higher than those adjacent to the main edge. The intensities of the dark and white bands do not follow any regular sequence.

INTRODUCTION

The X-ray absorption spectrum of sulphur was studied by Lindh[1] who observed the influence of chemical bindings on the positions of the primary K edges alone. But he did not investigate the nature of the extended secondary structures of the spectrum. He further noticed that the positions of the primary edge in monoclinic and rhombic varieties of sulphur were almost the same within the limits of experimental error whereas in the case of compounds the position depended on the valency of sulphur. The aim of the present investigation was to study the secondary structure of the absorption spectrum obtained with the various allotropic modifications of sulphur. Das[2] has recently found a new allotrope of sulphur (S_ω), of which the structure is not yet fully known. It was suspected that the mode of interatomic linkage inside a molecule of sulphur in the S_ω lattice is different from that present in orthorhombic crystals (S_α). In the latter type of crystalline sulphur, each molecule of sulphur contains eight atoms in a puckered ring. Now, we know that in the case of molecules possessing a large number of atoms, the secondary absorption spectrum does not depend much on the state of aggregation of these molecules. For, in these cases the intermolecular binding is so very strong in comparison with that between the molecules that the position of the energy levels (or allowed and forbidden energy zones) remain almost unaffected by the alterations of the mode of aggregation of the molecules. Thus one may expect that the sulphur molecules in S_α and S_ω really possess different stoichiometric structures, and this difference must also manifest itself in the secondary absorption spectra of these allotropes. With this idea, we took up the work which though still incomplete is being continued

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EXPERIMENT

As the soft X-rays lying in the region of the K-absorption spectrum of sulphur are very much absorbed by air, the effective path of the radiation in air was reduced by evacuating the spectrograph with the help of a Cenco Megavac Pump, and the tube was operated at 5 K. V. with a current varying from 25 to 50 milliamperes for different exposures which varied from 60 to 100 hours. The crystal used was Calcite and was oscillated through 2° 30′ by means of a specially devised arrangement. The slit through which the X-rays enter the Seigbahn spectrograph from the electron tube was 0·1 mm in breadth and was covered by very thin gold-beaters skin coloured red with magenta solution In this particular investigation the choice of the photographic films presented a great difficulty which was, however, overcome by trial. Several films and plates were tried but the intensity of the absorption bands even after an exposure of 90 to 100 hours with a current as high as 30 milliamp was not sufficient to produce a good contrast between the white and dark bands. Best results are obtained with doubly-coated Agfa Sino Films and Agfa Röntgen developer. The range through which the crystal is to be oscillated for obtaining all the absorption edges associated to the K-edge of sulphur (5008 X.U.) was first tested with the oscillation arrangement by photographing MoI_{β_1} (5041 X.U.) and MoI_{β_2} (4910 X.U.) on the same film. The reference lines, however, were taken to be 3 $NiK\alpha_1\alpha_2$ (4974 X.U.) and 2 $TiK\beta_1$ (5018 X.U.) emission lines.

PREPARATION OF ABSORBING SCREEN

The preparation of the absorbing screen caused the greatest trouble. The critical absorption wavelength of sulphur lies in the neighbourhood of 5 A.U. and the screen could not be prepared on ordinary paper or filter paper due to the high absorption by paper in this region of soft X-rays.. The substance was finely powdered in a mortar and uniformly spread by rubbing the powder between two ground glass plates when the sulphur stuck to one plate. On removing the upper plate, a dilute solution of celluloid in acetone was poured over it. When the thin film of celluloid was pulled off on drying, a uniform layer of sulphur stuck to the surface of the thin film of celluloid.

Other methods were also tried for the absorption screen of sulphur. In one method, the sulphur was finely powdered in a mortar and to the powder a little quantity of celluloid acetate solution was added. After preparation of an emulsion, the substance was allowed to pour on a clean glass plate levelled on a platform. On drying the film of celluloid, coated uniformly with sulphur, was obtained. But this method did not prove efficient as the one previously described

Another method of the preparation of the absorbing screen of sulphur is identical to the one first mentioned, the only difference being that instead of

TABLE I

Absorption Spectrum of Sulphur

The wavelengths are given in X.U.

	K	a_1	K_1	a_2	K_2	a_3	K_3	a_4	K_4	a_5	K_5	a_6	K_6	a_7	K_7	a_8	K_8	a_9
λ	5008·2	4998	4991	4981	4970	4960	4951	4949	4935	4924	4916	4895	4885	4875	4869	4858	4849	4840
			W		S		W	W				W			W	S	S	S
Δλ	0	10·2	17·2	27·4	38·2	48·2	57·2	59·2	73·2	84·2	92·2	113·2	123·2	133·2	139·2	158·2	159·2	168·2
ν/R	181·87	182·33	182·582	182·95	183·36	183·72	183·97	184·13	184·69	185·07	185·37	186·17	186·54	186·97	187·12	187·55	187·89	188·28
$\sqrt{\nu/R}$	13·486	13·503	13·512	13·526	13·541	13·553	13·564	13·57	13·59	13·604	13·615	13·64	13·658	13·674	13·679	13·695	13·686	13·77
$\Delta\nu/R$	0	·46	·70	1·08	1·49	1·85	2·10	2·26	2·82	3·20	3·50	4·20	4·67	5·12	5·25	5·68	6·02	6·42
ΔV	0	6·2	9·6	15	20	25	29	31	38·23	43	48·0	57	63	67	71	77	82	87

depositing them on the surface of thin films prepared by dissolving celluloid in acetone, the deposition was performed on a thin film prepared by dissolving collodion in a mixture of equal parts of alcohol and ether.

RESULTS

After several careful attempts with the orthorhombic variety (S_α) of sulphur, we were successful in obtaining one or two good absorption photographs which showed secondary structures extending over a large energy range on the short wavelength side of the primary. One of them is reproduced here (Fig. 1) where a large number of secondary edges is clearly visible. The wavelength and the usual values of λ, $\Delta\lambda$, ν/R, $\Delta\nu/R$, $\sqrt{\nu}/R$ and ΔV are given in the Table (1). The K, K_1, K_2 refer to the white lines and α_1, α_2, α_3, etc., denote the black bands, the primary edge being denoted by K.

No successful plate has yet been obtained with S_ω. In this case another additional difficulty is to be overcome. This is due to the unstable nature of S_ω. If the substance is seriously disturbed by heat or any mechanical operation as powdering, it transforms rapidly to insoluble S_α. So a special technique has to be devised for the preparation of the absorbing screen of S_ω.

Over and above the usual structures, another peculiarity is noticed in the photographic plate. It is found that over a certain range lying in the neighbourhood of the main edge, the general absorption is well marked, but at a certain point the intensity of absorption suddenly falls so that the whole range of absorption shows two distinct regions. The fluctuation of intensity and the general diffuseness of the band do not follow any regular sequence. The strong and weak absorption edges (both black and white) are marked by S and W in the Table. From measurements, the structures extend up to 87 volts from the primary edge. It may be mentioned here that this is for the first time that such an extended structure has been observed in the case of a lower element like sulphur. The positions of the bands were measured with a glass scale with 3 NiKα_1 and 2 TiKβ_1 as reference lines.

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REFERENCES

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PLATE III

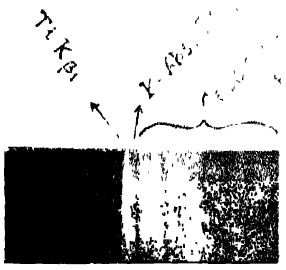

Fig.